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FTIR STUDY OF SiO_2 - TiO_2 XEROGELS

FTIR ANALÝZA SiO_2 - TiO_2 XEROGÉLOV

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Abstract

The SiO_2 - TiO_2 gels with three different molar ratios of TiO_2 and SiO_2 oxide were prepared by sol-gel method. After drying the prepared gels were heated at temperatures in range from 400 to 600 °C. The characterization of prepared xerogels is based on FTIR spectra analysis. Ti–O–Si bonds in SiO_2 - TiO_2 xerogels are formed during the formation of sol and during the heat treatment of xerogels. The formation of Ti–O–Si bonds has been confirmed by FTIR analysis of pure SiO_2 and TiO_2 xerogels and their mixtures.

Abstrakt

SiO_2 - TiO_2 gély s tromi rôznymi mólovými pomermi oxidov TiO_2 a SiO_2 sa pripravili metódou sól-gél. Pripravené gély sa po sušení vypaľovali pri teplotách v rozsahu 400 - 600 °C. Na charakterizáciu pripravených xerogélov sa využila FTIR spektrálna analýza. Zistilo sa, že v SiO_2 - TiO_2 xerogéloch sa Ti–O–Si väzby tvoria počas vzniku sólu a počas tepelného spracovania xerogélov. Vytvorenie Ti–O–Si väzieb sa potvrdilo aj FTIR analýzou "čistých" SiO_2 a TiO_2 xerogélov a ich zmesí.

Key words: sol-gel, xerogel, TiO_2, SiO_2, FTIR

1. Introduction

The sol-gel technique has been proven for several years now to be efficient for the processing of SiO_2 - TiO_2 materials. The materials from these oxides can be used for protective coating, antireflective coating, optical sensor application, catalysts etc. Titania-silica materials not only take advantage of both TiO_2 and SiO_2, but also extend their application due to the interaction of TiO_2 with SiO_2. There are two types of interaction between TiO_2 and SiO_2: physically mixed (with interaction forces being nothing more than weak Van der Waals forces) and chemically bonded (i.e., the formation of Ti–O–Si linkages) [1]. The degree of interaction largely depends on preparation methods, synthesis conditions etc. Sol-gel process has possible capability in controlling the textural and surface properties of the mixed oxide.

The simplest way to examine the formation of Ti–O–Si bonds in SiO_2 - TiO_2 mixed oxides is to use Fourier transform infrared (FTIR) spectroscopy. The IR bands observed at 910 - 960 cm^{-1} is widely accepted as the characteristic vibration due to the formation of Ti–O–Si bonds, with the exact band position depending on the chemical composition of the sample as well as calibration and resolution of the instrument. The intensity of this IR band has been used to evaluate the absolute amount of Ti–O–Si linkages [1].

The work presented in this paper is based on FTIR spectra analysis. Its aim is to study of the evolution with heating temperature of the chemical composition and structure of prepared xerogels.

2. Experiment

Procedure details of the preparation of pure TiO_2 and SiO_2 xerogels have previously been given in reference [2]. In brief, two kinds of sols were prepared in order to obtain mixed SiO_2 - TiO_2 xerogels. The TiO_2 sol was prepared by diluting titanium tetra-isopropoxide ($Ti(iPr)_4$) with acetylacetone (AcAc) in isopropylalcohol (IPA), distilled water (H_2O) and nitric acid (HNO_3). The SiO_2 sol was prepared by diluting tetraethoxysilane (TEOS) in isopropylalcohol, water and nitric acid. Both sols were aged at laboratory temperature for 1 hour. The TiO_2 sol was then added dropwise to the above SiO_2 sol under magnetic stirring within 15 minutes. The molar composition of the sols is showed in Table 1. The solutions thus prepared were dried at temperature 80 °C to the constant weight. Then, the xerogel samples were heat treated in air at temperatures of 400, 475, 500, 525 and 600 °C. The xerogels were heated by the rate of 10 °C/min and maintained at the desired temperature for 120 minutes.

Table 1 The molar composition of sols

Sample	TEOS	$Ti(iPr)_4$	IPA	HNO_3	H_2O	AcAc
T	0	1	20.82	0.78	0.60	2.12
S1T2	1	2	56.95	1.67	5.12	4.24
S1T1	1	1	36.13	0.89	4.52	2.12
S2T1	2	1	51.45	0.99	8.44	2.12
S	1	0	15.31	0.11	3.92	0

FTIR spectra were recorded in a FT-IR Bomem spectrometer with 4 cm^{-1} resolution in the wavenumber range of 4000 - 400 cm^{-1}. Samples were grounded, mixed with KBr and pressed to tablet form. Concentrations of the samples in tablets were kept around 3 wt. %.

For comparison of FTIR results of prepared SiO_2 - TiO_2 xerogels, the samples with same molar ratios of SiO_2 : TiO_2 oxides were prepared from pure TiO_2 and SiO_2 xerogels. These samples were prepared by mixing of required amounts of pure TiO_2 and SiO_2 xerogels, which were heated at 400, 525 and 600 °C.

3. Results and discussion

Figures 1 and 2 show the FTIR spectra of pure TiO_2 and SiO_2 xerogels heated at various temperatures. The absotption band near 1640 cm^{-1} is attributed to the bending vibration of H–O–H bonds, which is assigned to the chemisorbed water [3].

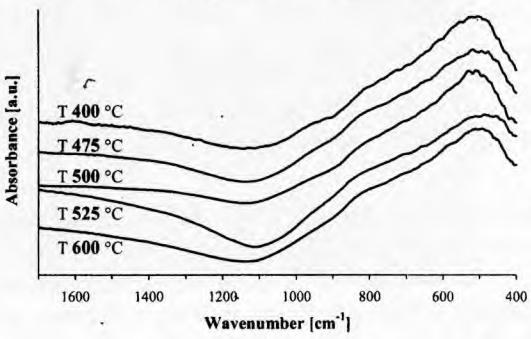

Fig. 1 The FTIR absorbance spectra of pure TiO2 heated at various temperatures.

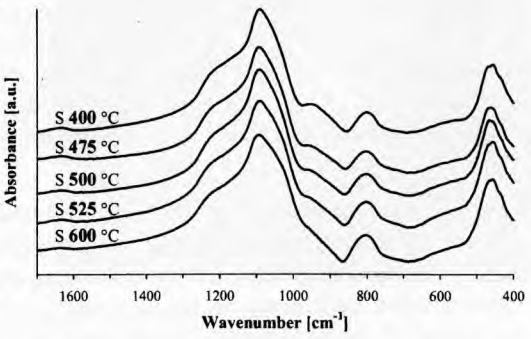

Fig. 2 The FTIR absorbance spectra of pure SiO2 heated at various temperatures.

Ti–O–Ti bonds appeared in the range 400 - 600 cm^{-1} for pure TiO_2 [1]. The influence of temperature is not very significant in spectra of pure TiO_2. The peak around 670 cm^{-1} represents Ti–O–Ti [4] and/or Ti–O bonding [5].

Fig. 2 shows the characteristic bands usually observed in SiO_2 materials. Dominant band near 1085 cm^{-1} is associated to asymmetric stretching vibration ν_{AS}(Si–O–Si). This band is accompanied by strong shoulder on the side of higher wavenumber (near 1200 cm^{-1}) [6]. Absorption band near 950 cm^{-1} is mostly associated to mode ν(Si–OH) and/or Si–O$^-$ stretching vibration [6, 7]. Bands near 800 cm^{-1} and 460 cm^{-1} are assigned to symmetric stretching vibration ν_S(Si–O–Si) respective deformation ρ(Si–O–Si) [6, 7]. The IR spectra on Fig. 2 clearly show the evolution of SiO_2 xerogel with heating temperature. The intensity of the ν_{AS}(Si–O–Si) and ρ(Si–O–Si) vibrations increases when increasing the temperature, while the Si–OH, resp. Si–O$^-$ band decreases.

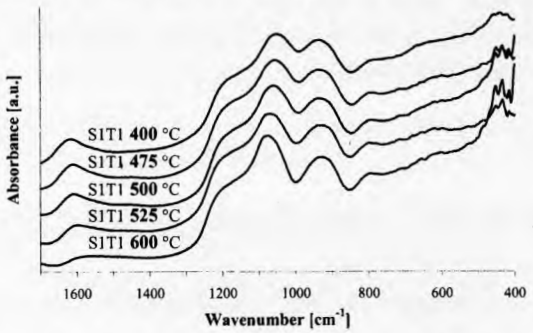

Fig. 3 The FTIR absorbance spectra of SiO_2 - TiO_2 (1:1) xerogel heated at various temperatures.

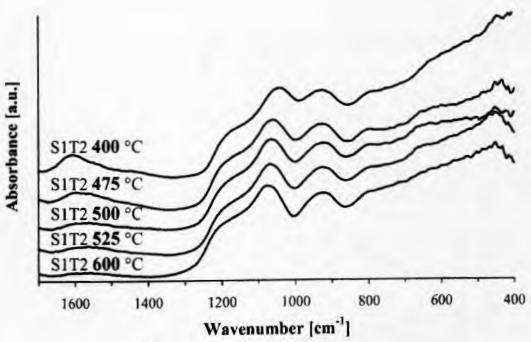

Fig. 4 The FTIR absorbance spectra of SiO_2 - TiO_2 (1:2) xerogel heated at various temperatures.

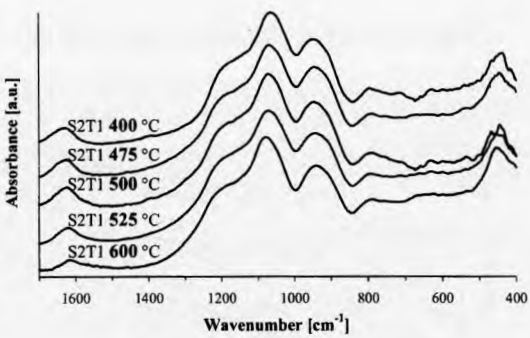

Fig. 5 The FTIR absorbance spectra of SiO_2 - TiO_2 (2:1) xerogel heated at various temperatures.

The FTIR spectra of three SiO_2 - TiO_2 xerogels heat-treated at various temperatures are presented in Figures 3 - 5. In these spectra the stronger absorption band approximately 1060 cm^{-1} is assigned to the vibration of Si–O–Si bonds. The band approximately 600 - 700 cm^{-1} represents Ti–O–Ti bonding [4] especially in samples with higher content of TiO_2 (Fig. 3 and 4). The band approximately 450 cm^{-1} presumably corresponds to Ti–O–Ti [8, 9] and Si–O–Si bonds [5]. This band increases in intensity when the content of TiO_2 increases.

The absorption band approximately 900 - 1000 cm^{-1} is attributed to the stretching vibration of Si–OH and Si–O$^-$ specious and Ti–O–Si bonds [9, 10]. This band is a result of overlapping of the bands due to Si–OH, resp. Si–O$^-$ and Ti–O–Si. The position of this band is 935 cm^{-1} in the SiO_2 -

TiO_2 (2:1) xerogel and 920 cm^{-1} in the SiO_2 - TiO_2 (1:2) xerogel. The intensity of the characteristic band for the Ti–O–Si bonds increases with increasing heat treatment temperature. The intensity trend indicates that the amount of Ti–O–Si bonds is the same or increasing in all SiO_2 - TiO_2 samples when heat treatment temperature is in the 400 - 600 °C range. Assignment of band to Ti–O–Si bonds is confirmed on the base of the comparison of FTIR spectra of SiO_2 - TiO_2 xerogels with mixed xerogels prepared from pure TiO_2 and SiO_2 xerogels (Figures 6 - 8). The broad band, approximately 400 - 600 cm^{-1}, corresponds to Ti–O–Ti bonds in all mixed xerogels and all temperatures. The intensity of the absorption band at 1090 cm^{-1} decreases with increasing of SiO_2 content, and according to this fact can be deduced that this band corresponds to asymmetric stretching vibration of Si–O–Si. There isn't practically any band in range of 900 - 1000 cm^{-1} in mixed xerogels. It means, that there is only few or there are not any Ti–O–Si bonds in samples prepared by mixing of pure TiO_2 and SiO_2 xerogels. This fact indicates that Ti–O–Si bonds are formed by chemical reaction during sol preparation. This implication is confirmed by FTIR spectra of pure SiO_2 xerogel on the base of changes of Si–OH and Si–O^- band at 950 cm^{-1}, which intensity was decreased when the heating temperature was increased (Fig. 2). Development of characteristic Ti–O–Si band indicates that Ti–O–Si bonds are formed during heat treatment.

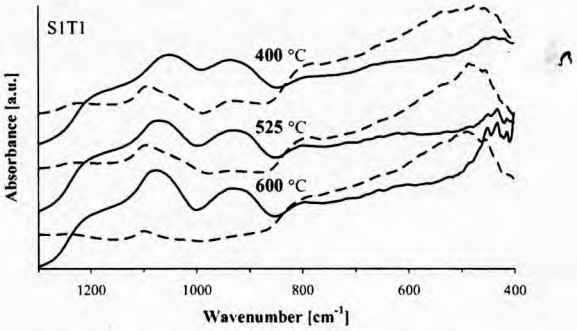

Fig. 6 The FTIR absorbance spectra of SiO_2 - TiO_2 (1:1) xerogels (–) and mixed xerogels (- -).

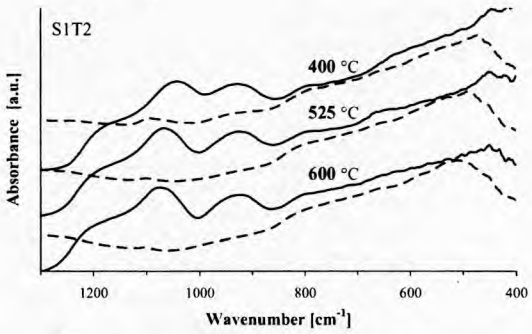

Fig. 7 The FTIR absorbance spectra of SiO_2 - TiO_2 (1:2) xerogel (–) and mixed xerogels (- -).

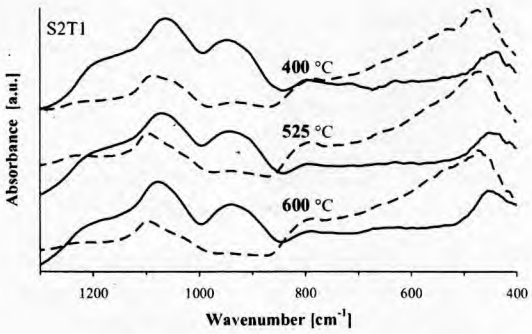

Fig. 8 The FTIR absorbance spectra of SiO_2 - TiO_2 (2:1) xerogel (–) and mixed xerogels (- -).

4. Conclusion

Three SiO_2 - TiO_2 xerogels with different molar ratios of TiO_2 and SiO_2 oxide were prepared by sol-gel method. FTIR spectroscopy has shown that the Ti–O–Si bonds are formed during the formation of sol and the heat treatment of xerogels. FTIR analysis of pure SiO_2 and TiO_2 xerogels and their mixtures have confirmed this implication.

Acknowledgement

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